Polymerization of *N*-Vinylcarbazole by Chlorides and Oxychlorides of Some Group V Elements. I. Polymerization by $POCl_3$, $AsCl_3$ and $SbCl_3$

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In the course of our studies[1-3] on initiator systems for *N*-Vinylcarbazole (NVC) polymerization we have observed that $POCl_3$, $AsCl_3$ and $SbCl_3$ can effectively initiate the solution polymerization of NVC. This communication reports our preliminary observations on these systems.

Polymerization was carried out under nitrogen at 30°C with purified and dry reagents. Conversion at intervals of 2, 4, 6 and 8 up to 30 min was followed gravimetrically after purifying the polymer.[3] Molecular weights ($\bar{M}_n$) were determined cryoscopically in benzene. Polymer melting points were >350°C.

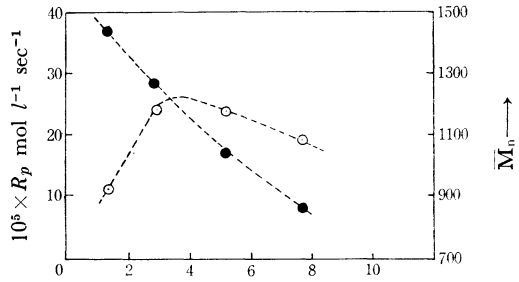

Fig. 1. Dependence of R_p on [NVC] (⊙) and of $\bar{M}_n$ on [NVC] (●); $[AsCl_3] = 16.2 \times 10^{-4}$ M.

For NVC-$AsCl_3$-benzene system, R_p was first order in $AsCl_3$ concentration. The variation of R_p and $\bar{M}_n$ with NVC concentration is shown in Fig. 1. With NVC-chloranil-nitrobenzene system, Pac and Plesch[4] found a maximum by plotting specific rate constant against NVC concentration. Dependence of the maximum on $AsCl_3$ concentration is being investigated. We feel that increased termination and transfer may be important, but any definite comment on this trend would not be justified at this stage.

The reactions were usually exothermic. R_p of NVC-$AsCl_3$ system was dependent on solvent dielectric constant (Fig. 2) and so was $\bar{M}_n$ (1269 in benzene and 3982 in nitrobenzene, for example). Additives such as water, dimethylaniline, aniline and triethylamine related the rate. These features suggest a cationic mechanism.

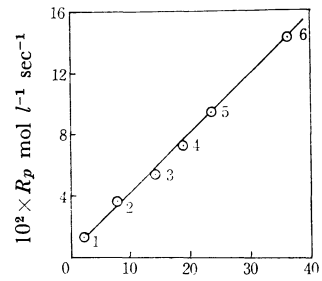

Fig. 2. Dependence of R_p on solvent dielectric constant. $[NVC] = 0.29$ M; $[AsCl_3] = 16.2 \times 10^{-4}$ M; (1) B (100%); (2) 75% B+25% NB; (3) 50% B+50% NB; (4) 37.5% B+62.5% NB; (5) 25% B+75% NB; (6) NB (100%). (B=Benzene; NB=Nitrobenzene). Values of solvent dielectric constant taken from Ref. 5.

Some experiments were performed with $POCl_3$ and $SbCl_3$. Thus $POCl_3$ (0.063—0.19 M) and NVC (0.77 M) produced (30°C; benzene; 1320 min) 94% deep yellow orange poly NVC, $\bar{M}_n$: 2704, mp >350C°. $SbCl_3$ (0.068 M) and NVC (0.29 M) produced (30°C; benzene; 765 min) 74% white poly NVC, $\bar{M}_n$: 2254, mp >350°C.

In a few cases a colour change was noted during reaction. With NVC-$Fe(NO_3)_3$, $9H_2O$ system Okamura *et al.*[6] reported a similar colour change. In our case this colour change was not a necessary condition for polymerization. In fact, colour could be produced by mixing poly NVC with $AsCl_3$ in benzene. This latter observation may be related to the possibility of charge transfer interaction between poly NVC and $AsCl_3$. Interaction between poly NVC and acceptors such as $SbCl_5$ is known.[7] Spectrophotometric investigations are in progress.

Details of all these observations will appear in due course.

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